

Magnetic properties of $3d$ -impurities substituted in GaAs

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We have calculated the magnetic properties of substituted $3d$ -impurities (Cr- Ni) in a GaAs host by means of first principles electronic structure calculations. We provide a novel model explaining the ferromagnetic long rang order of III-V dilute magnetic semiconductors. The origin of the ferromagnetism is shown to be due to delocalized spin-uncompensated As dangling bond electrons. Besides the quantitative prediction of the magnetic moments, our model provides an understanding of the halfmetallicity, and the raise of the critical temperature with the impurity concentration.

As the electronic device sizes are shrinking, physicists are asked to provide new device concepts. Devices that work, not despite quantum mechanics but because of quantum mechanics. One track is the area of magnetoelectronics, where one in addition to the charge of the electron tries to exploit its spin degree of freedom¹. A central problem is here the spin injection into the semiconductor, i.e. a diluted magnetic semiconductor (DMS), for the spin injection is now being worked on worldwide³. So far, the mechanism for the ferromagnetic long range order in DMSs has been a matter of dispute. Akai⁴ and more recently Dietl et al.⁵ proposed the double-exchange mechanism to explain the ferromagnetic order.

In this letter, we propose a novel mechanism for the ferromagnetism of DMSs. We show that the ferromagnetic order is caused by itinerant spin-uncompensated As dangling bond (DB) states: The $3d$ -impurity atom interacts with the As DBs. Because of the spin-polarization of the $3d$ -atom, the hybridization with the spin-up As DBs is larger than with the spin-down ones. This has two consequences: i) Since the DB states are delocalized, the hybridization leads to an itinerant magnetic moment. ii) The filling of the As DBs remains incomplete. An eventual filling of these holes destroys the ferromagnetic order in agreement with experiment⁶.

To support our analysis we perform *ab initio* calculations of Ga-substituted impurities (Cr, Mn, Fe, Co, and Ni) in a GaAs host. The magnetic properties were calculated using a plane wave pseudopotential code (VASP^{7,8}) within the local spin density approximation

(LSDA)⁹. The atoms are described by ultra soft Vanderbilt type pseudopotentials¹⁰ as supplied by G. Kresse and J. Hafner¹¹. The wave functions are expanded in plane waves with an energy cut-off of 295 eV. The electron density was calculated using special \mathbf{k} -point sets¹² corresponding to a $2 \times 2 \times 2$ folding. The resulting number of \mathbf{k} -points was shown to be sufficient for the here studied properties. The calculations are performed within a 64 atom supercell, where the $3d$ -atom is put on a Ga-site in the center of the cell.

In Fig.1 we show the spin-resolved d -projected density of states (DOS) at the impurity site. For the unrelaxed case (left column), i.e. all atoms are sitting on ideal high symmetry positions, GaAs containing Cr, Mn, or Co (Fe or Ni) impurities has become a half-metal (metal). In the right column of Fig.1 we show the results for the position, volume, and shape relaxed case. For Cr or Mn impurities in GaAs, the effect of the relaxation is negligible, whereas for Fe, Co, and Ni the relaxation almost suppresses the ferromagnetism. Co or Ni impurities in GaAs are non-magnetic, for Fe in GaAs the magnetic moment has drastically decreased (Fig.2).

In order to understand these *ab initio* results, we apply an "impurity-molecule model"^{13,14} which we develop in three steps. i) We consider the ideal, i.e unrelaxed, GaAs host with a Ga vacancy. At the vacancy site the four surrounding As neighbours contribute five electrons to the four DBs. We calculate the Ga-vacancy to be non-magnetic. The site-projected vacancy DOS is shown in Fig.3. Close to the Fermi energy (E_F) a split peak appears in the DOS of the Ga-vacancy (bottom panel of Fig.3). The two peaks have the following origin: Three As DBs give rise to the peak at E_F (three top panels), whereas one As DB gives rise to the peak below E_F (panel four of Fig.3). We conclude, that the occupation of the As DBs is as follows: One DB is completely occupied (peak below E_F) and three DBs are only half-occupied (peak at E_F).

In total the vacancy has 3 holes, i.e. there are 1.5 holes per spin. In a tetrahedral crystal field the sp^3 orbitals split into " s " -like a_1 orbitals and " p " -like t_2 orbitals¹⁴. At the vacancy site the a_1 state is completely filled and the t_2 states have 3 holes. The t_2 state of the Ga vacancy is located 0.06eV above the valence band edge and is thus almost degenerate with the continuum of extended states¹⁵. The Ga vacancy t_2 state can thus be treated as a delocalized state. Only then the nonmagnetic state of the vacancy is understandable.

ii) Next the vacancy is filled with the $3d$ -impurity. In

a tetrahedral crystal field the d -states are split into e and t_2 states, where the e states lie lower in energy than the t_2 states¹⁶. For all $3d$ impurities (with the exception of Ni) only the spin-up t_2 (t_2^\uparrow) states are occupied, i.e. the t_2^\downarrow states are completely empty. We assume that the impurity retains its atomic character, i.e. the occupation of the e and t_2 levels follows Hund's rules.

iii) Finally, we consider the interaction of the $3d$ impurity with the four As DBs. It is well known that a substitutional impurity in a semiconductor is ionized so that the semiconductor holes become filled. One would thus expect the $3d$ -atom to contribute 3 electrons to the hole-filling, i.e a $3+$ -state of the $3d$ impurity. However, for a spin-polarized impurity there are two possibilities: (1) If the exchange energy is larger than the energy gain (bonding energy) due to the complete hole filling of the As DBs, only the spin-up channel will interact with the As DBs, i.e a spin-flip on the $3d$ impurity site is prohibited. (2) If, in contrast to the first possibility, the bonding energy exceeds the exchange energy, 3 electrons will be transferred to the As DBs, i.e a spin-flip on the $3d$ impurity site is allowed. In the following, we will discuss the two cases separately.

First assume case (1), i.e that the exchange energy exceeds the bonding energy. This case agrees with the results for the unrelaxed first-principles calculation. Due to their like symmetry and large overlap, only the t_2^\uparrow states of the impurity and the As DB hybridize. Therefore the $3d$ -impurity contributes only 1.5 spin-up electrons to the hole-filling of the As DBs. Because the $3d$ impurity states are localized, not 1.5 but an integer number of two electrons are promoted to the Fermi energy, of which 0.5 electrons have a high probability to be found on the impurity site itself. Thus one electron is shared between the impurity and the delocalized As DBs. The occupation of the impurity atom t_2^\uparrow level is therefore reduced by two electrons (states), i.e. the $3d$ atom assumes a $2+$ state. In the following we discuss this charge transfer in more detail:

The As DBs receive 1.5 t_2^\uparrow electrons. In order to minimize the energy (especially the kinetic energy of the host), it seems at first sight, that the optimal situation would be to equally distribute the 1.5 electrons on both spin-channels of the host, i.e. 0.75 electrons had to spin flip. But, this apparently optimal situation is not allowed, because of the following: On the impurity site only spin-up states are available at the Fermi energy (due to the exchange splitting of the d-states). Since, as mentioned above, one promoted electron is shared between the impurity atom and the delocalized As DBs, the spin of one of the two promoted electrons is restricted to be spin-up. In order to minimize the energy, only one electron of the 1.5 transferred t_2^\uparrow electrons, is allowed to be equally distributed among both spin-channels, i.e. only 0.5 electrons are allowed to spin flip. In total then, the spin-up (spin-down) channel of the host has received 1.0 (0.5) electron.

An alternative discussion of the charge transfer is the following: Let us start from the vacancy dangling bonds. As mentioned earlier, three orbitals of the four delocalized As DBs, are half occupied (0.5 electron per spin) and one orbital is completely occupied (1 electron per spin) , because five electrons have to be redistributed on four DBs). Assume now that we add one electron to the vacancy and distribute it equally among both spin channels. Adding 0.5 electrons to each spin channel of the As DBs, gives rise to the following occupation of the As DBs: three orbitals are completely occupied (1 electron per spin) and one orbital is completely empty (0 electron per spin), because six (five plus one) electrons have to be redistributed on four DBs. This is an energetically very favorable situation, because the DOS at the Fermi energy is drastically reduced to zero, i.e. a bandgap exists. The $3d$ -impurity donates to the As DBs 1.5 t_2^\uparrow electrons, of which one is used to create the bandgap as described above. Now, because not only one electron, but 1.5 t_2^\uparrow electrons are transferred form the impurity to the As DBs, the spin-up channel of the As DBs receives an additional 0.5 electron. Therefore the spin-down channel has a bandgap, whereas the spin-up channel has one partly occupied orbital, i.e a state at the Fermi energy (Fig.1). This additional 0.5 electron corresponds to one half of the shared electron. This discussion also shows, that any other distribution of the 1.5 t_2^\uparrow electrons within the As DBs, will increase the total energy, because the bandgap in the spin-down channel would have to disappear.

In total the impurity has lost 1.5 spin-up electrons and the As DBs have gained 0.5 spin-down electrons and 1.0 spin-up electrons. Hence the occupation of the spin-up As DBs exceeds the occupation of the spin-down As DBs by 0.5 electrons and this spin-imbalance is accompanied by an *itinerant* magnetic moment, $M_{itinerant} = 0.5\mu_B$. Note, that although this amounts to a relatively small moment per formula unit, it constitutes the origin of the long range order, i.e the ferromagnetism of the DMS. Our model also gives a natural explanation for the observation of so called "hole mediated ferromagnetism"⁶. Namely, any spin-imbalance (ferromagnetism) will be quenched, if the remaining 1.5 holes of the As DBs are filled (disappear) for instance by additional donor-dopants.

We can now express the (local) magnetic moment at the impurity site simply as follows:

$$M_{local} = d^\uparrow - d^\downarrow - N, \quad (1)$$

where N is equal to 1.5 (unrelaxed case), and d^\uparrow, d^\downarrow correspond to the d-occupation of the impurity atom.

The total magnetic moment per impurity atom, M_{total} , is the sum of the local and itinerant moment:

$$M_{total} = M_{local} + M_{itinerant} = d^\uparrow - d^\downarrow - 1. \quad (2)$$

In the case of, for example, (Ga,Mn)As, the local Mn magnetic moment amounts to $M_{local} = 5 - 0 - 1.5 = 3.5\mu_B$ and M_{total} amounts to $4\mu_B$. In Fig.2 we summarize our results for Cr, Mn, Fe, Co, and Ni impurities

in a GaAs host. We compare our model (Eq.1-2) with the self consistently calculated magnetic moments. For the unrelaxed case (left column) discussed so far, one notices an overall agreement with some deviations, which however can be explained easily. For Cr and Mn the total magnetic moment agrees perfectly, whereas the itinerant magnetic moment is smaller by about $0.2\mu_B$ and the local magnetic moment is larger by the same amount than predicted by our model. In our model, we assumed one electron to be shared equally between As and the 3d-impurity. Realizing that due to the difference in electronegativity, more than half of the shared electron is located on the impurity site, the deviations are obvious and follow the expected chemical trend.

The other deviation we find for Ni and Fe. This can also be easily understood from the calculated d - and site-projected densities of states (Fig.1). For Fe and Ni we do find spin-down states at the Fermi energy: in case of Fe these are e^\downarrow states and in case of Ni t_2^\downarrow states. These additional states contribute to the minimization of the total energy and are for simplicity neglected in our model, though it is straight forward to expand the model.

Now we compare our model with the calculated DOS (Fig.1). In agreement with our model, we find two important features in the spin-up channel: (1) one deep lying broad feature originating from the localized t_2 and e -states on the impurity site ($E \sim 1.7\text{eV}$). For Cr this broad feature does not exist, because the Cr atom only has 2 t_2 electrons. Thus for Cr there is an additional empty t_2 peak above the Fermi energy. (2) one double t_2 -peak close to the Fermi energy originating from the shared electron between the Ga-vacancy and the impurity.

So far we have not considered any relaxations that increase the overlap between the As DBs and the impurity t_2 states. With an increased overlap, the gain in bonding energy, E_{bo} , might become larger than the energy gain due to the exchange splitting, E_x . Then 3 electrons of the 3d-impurity hybridize with the As DBs, because the cost to spin-flip 1.5 d-electrons (of the impurity) is compensated by the gain in bonding energy. Therefore the impurity will undergo a transition from a high-spin state to a low-spin state. A similar discussion for 3d transition metal ions in Si has earlier been given by Beeler et al.¹⁷. For Cr and Mn the exchange energy is large and there are no spin-down states at the Fermi level into which a t_2 spin up electron could flip. The system therefore would loose energy when increasing the overlap between As and Cr (Mn). That is why the As-Cr and As-Mn bond length is more or less maintained.

For Fe, Co and Ni on the other hand, the system gains energy, when 1.5 t_2 electrons spin-flip to fill all As DB holes, and consequently the bond length is thereby decreased by about 7 %. (Co,Ga)As and (Ni,Ga)As are non-magnetic, whereas M_{total} amounts to $1\mu_B$ for (Fe,Ga)As. Our model ($N=3$ in Eq.1) predicts for Fe a local magnetic moment of $1\mu_B$, but a zero itinerant mag-

netic moment. With our first principles calculations we find an itinerant moment of $0.2\mu_B$ and a local moment of $0.8\mu_B$. This difference is explained as follows: Due to the difference in electronegativity between Fe and As, some of the delocalized electrons become localized on the Fe site. Since the e^\downarrow states at the Fermi energy are completely filled, only spin-down electrons can get localized at the Fe site. It follows, that the local magnetic moment is reduced by the amount, A , of localized spin-down electrons. From Fig.2 one would expect an A between -0.1 and -0.2 μ_B . This in turn leaves an itinerant magnetic moment of $A\mu_B$, in agreement with our first principles calculations. We thus find the ferromagnetism of (Fe,Ga)As to be independent on the number of holes in the DMS.

In order to understand the increase of the critical temperature, T_c , with the increase of the Mn impurity concentration⁶, consider the following: The itinerant magnetic moment per host atom increases with Mn concentration, whereas the total magnetic moment per impurity atom is independent on Mn concentration. Because in our model only the itinerant magnetic moment is responsible for the long range order, we assume T_c to be proportional to the itinerant magnetic moment. Accordingly, T_c increases with Mn concentration.

Recent theoretical calculations on (Ga,Mn)As report the As nearest neighbour (nn) local magnetic moment to be antiparallel to Mn^{18–21}. But this does not contradict with our model as we will illustrate in the following: First, notice that the spin down channel of the As DBs is more localized than the spin up channel, because of the following reason: The 0.5 additional electrons in the spin-up channel shifts the spin-up DB states deeper into the valence band, and hence increases its resonance with the valence band, and in effect the spin up DB states become more delocalized.

Second, it thus follows that on the As nn sites, the local As moment might be determined by the spin down channel and accordingly the local As moment may be antiparallel to the impurity moment. The sign of the local As moment depends thus on the chosen local sphere radius. The smaller the chosen sphere radius, the more negative becomes (also in our calculations) the local As moment. However, most important, these recent calculations confirm the existence of an integer total magnetic moment and a non-integer local moment at the impurity site.

Experimentally, often a magnetic moment of $5.0\mu_B$ is measured for (Ga,Mn)As. We did a calculation where we add one electron to the unit cell which becomes charge compensated by a jellium background. In this way we simulate the electronic effect of additional dopants in the unit cell, whose defect-level(s) determine the Fermi level to lie above the pure (Ga,Mn)As Fermi energy. We find a total moment of $5.0\mu_B$ and a local moment of $4.0\mu_B$. Within our model this is understandable in the following way: Adding one electron, the vaccancy has instead of 3 only 2 holes, i.e. one hole per spin. The energetically most stable situation is with 3 fully occupied

orbitals and one empty orbital. Out of the 5 spin-up d-electrons now only one electron is transferred to the As DBs. This electron will maintain the spin, because the system would loose energy, when both (spin-up and spin-down) empty orbitals would become filled by half an electron. Moreover, this transferred spin-up electron is delocalized, i.e the itinerant moment is $1.0\mu_B$. Therefore, the Curie temperature of the negatively charged Mn impurity should be higher than of the neutral Mn impurity.

In summary, the present model explains the ferromagnetic long range order as being caused by itinerant spin uncompensated t_2 orbitals. The simultaneous occurrence of an itinerant and local magnetic moment is explained. Our model quite naturally explains the halfmetallicity of (Ga,Mn)As. Moreover, because the itinerant moment per host atom increases with the impurity concentration, our model explains the dependence of T_c on the impurity concentration.

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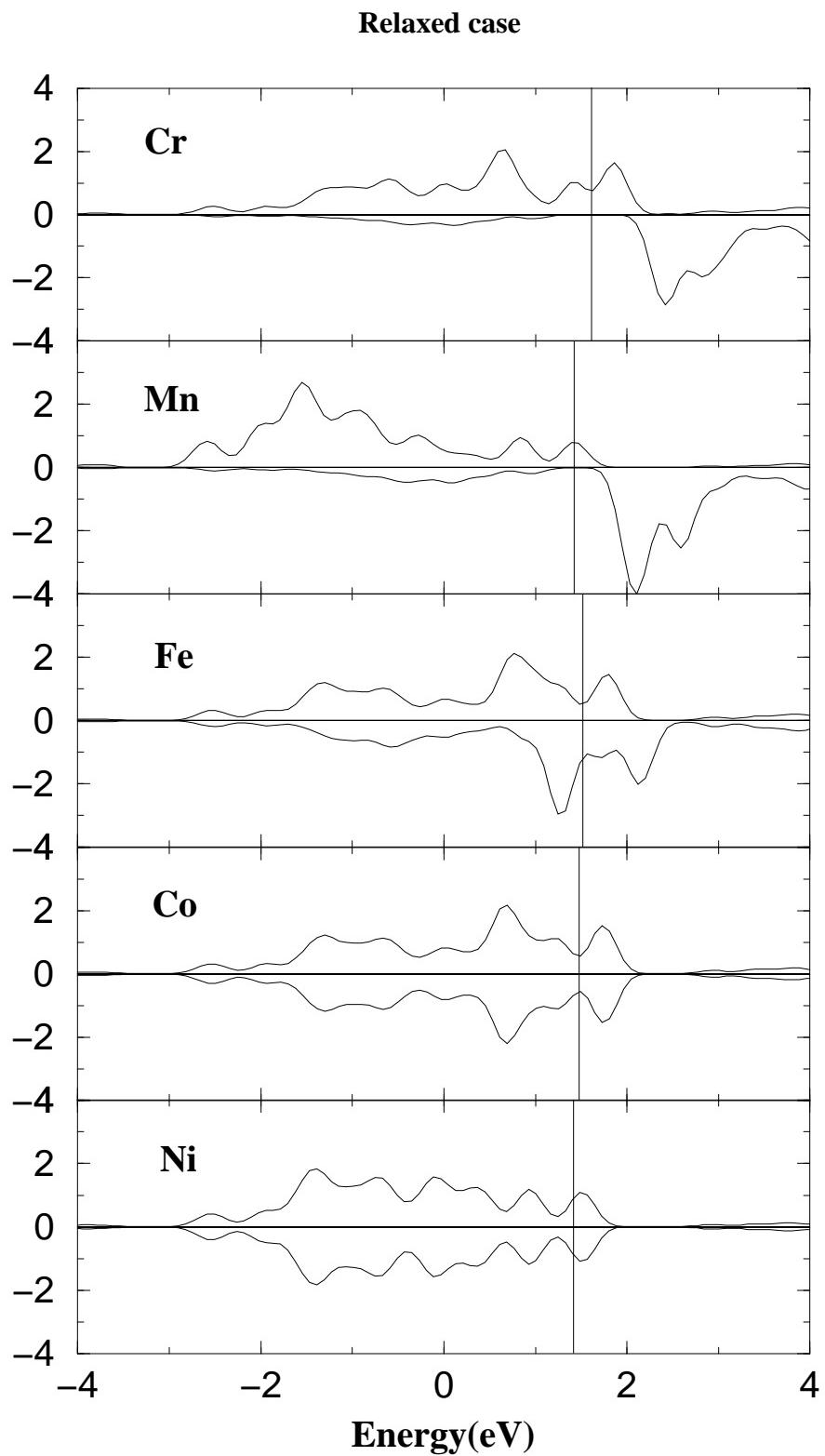
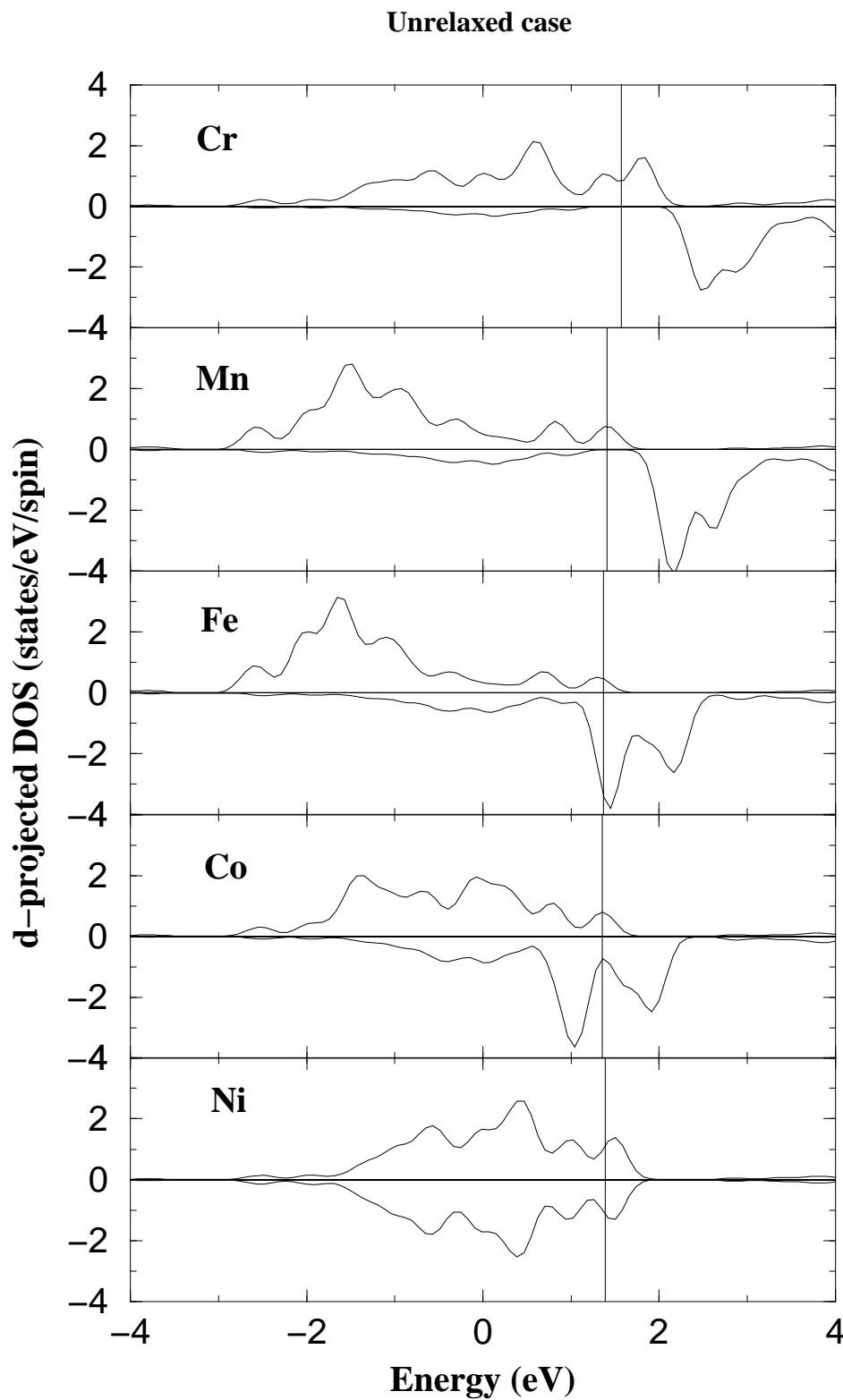
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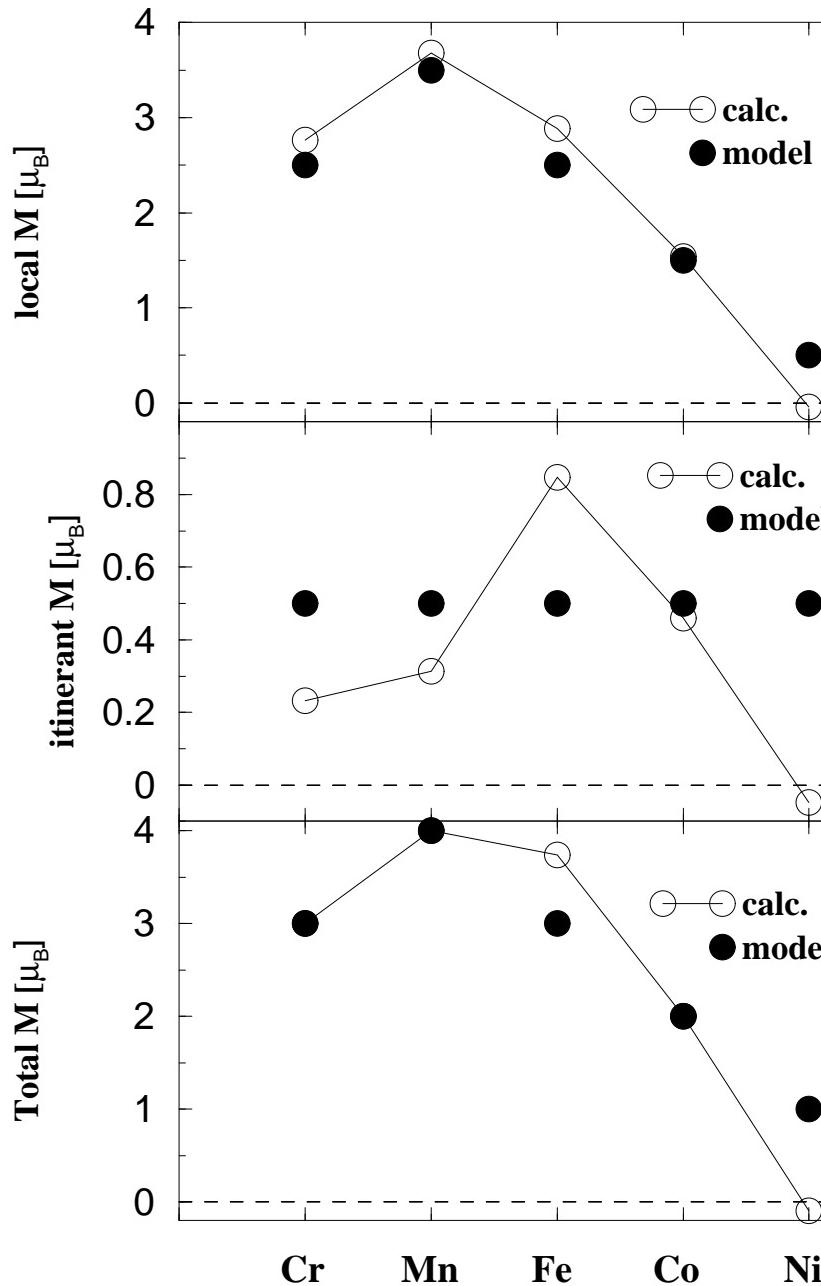
FIG. 1. Calculated d -density of states projected onto the $3d$ -impurity site. The left (right) column shows the DOS for the unrelaxed (relaxed) case. The vertical lines indicate the position of the Fermi energy.

FIG. 2. Comparison of the calculated magnetic moments and the model predictions. The left (right) column shows the unrelaxed (relaxed) case. In the first row we show the local magnetic moment, in the second row we show the itinerant magnetic moment, and in the last row we show the total magnetic moment.

FIG. 3. Calculated DOS for the unrelaxed vacancy: The four top panels show the p -DOS projected onto the four nearest As neighbours (AsI, AsII, AsIII, AsIV) of the vacancy. The bottom panel shows the sum of the p -DOS of the four As neighbours.



Unrelaxed case



Relaxed case

